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Complexation of Eu(III) with alkyl-substituted malonamides in acetonitrile

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The complexation of Eu(III) with a series of alkyl-substituted malonamide ligands was studied in organic solvents using calorimetry, FT-IR and luminescence spectroscopy. The formation constants were determined in acetonitrile containing small amounts of dimethyl sulfoxide. The effects of substitution on the nitrogen atoms as well as on the central carbon atom were evaluated. For the substitution on the nitrogen atoms, the formation constants decrease in the order: *N*,*N*,*N*′,*N*′-tetramethylmalonamide (TMMA) > *N*,*N*′-dibutyl-*N*,*N*′-dimethylmalonamide (DMDBMA) > *N*,*N*,*N*′,*N*′-tetrahexylmalonamide (THMA) > *N*,*N*,*N*′,*N*′-tetraisopropylmalonamide (TiPMA). For substitution on the central carbon atom, the formation constants decrease in the order: *N*,*N*,*N*′,*N*′-tetrahexyl-2-methylmalonamide (MeTHMA) > *N*,*N*,*N*′,*N*′-tetrahexylmalonamide (THMA) > *N*,*N*,*N*′,*N*′-tetrahexyl-2,2-dimethylmalonamide (DMeTHMA). These orders are discussed in terms of the steric effect and the ligand basicity.

1 Introduction

Alkyl-substituted amides have been the focus of numerous studies because they could be used as alternative extractants to organophosphorus compounds for actinide separation.[1–7] Studies have shown that they are effective either used alone[4–6] or with β-diketones in synergistic extraction.[7] Compared to organophosphorus compounds, back extraction of actinides from the amide-containing organic solvents is relatively easy. The products of radiolytic and hydrolytic degradation of amides are less detrimental to separation processes than those of organophosphorus compounds. In addition, the amide ligands are completely incinerable, which implies that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced.[2,3,8,9]

Most of the studies on amides have been focused on the determination of distribution coefficients,[10–16] a good measure of their effectiveness in extracting actinides under particular experimental conditions. However, since the extractions were conducted under different conditions, a systematic comparison between different amides is usually difficult. To understand the nature of the metal–amide binding and predict the effectiveness of amides as extractants, some recent studies are focused on the coordination chemistry of metal/amide complexes and have provided useful information on the structure–function relationship.[6,17–22] For example, Chan *et al.*[6] and Spjuth *et al.*[18] found that *N*,*N*′-dimethyl-*N*,*N*′-diphenyltetradecylmalonamide (DMDPHTD) is a good extractant, because the O=C · · · C=O torsion angle of the ligand is small so that only a small conformational change is required to form the metal complex. Lefrançois *et al.*[19] demonstrated by NMR that the rotation barriers of malonamides are dependent on the bulkiness of substitutional groups. In a previous work from this group[22] it is observed that *N*,*N*,*N*′,*N*′-tetramethylmalonamide (TMMA) forms stronger complexes with Eu(III) than *N*,*N*,*N*′,*N*′-tetramethylsuccinamide (TMSA). The difference in the binding affinity between TMMA and TMSA is attributed to the steric strain induced by complexation and an entropy effect due to the variation in the length of the carbon backbone. In summary, these studies have demonstrated that the structural variations of the diamides, such as the substituents and the length of the carbon chain, have a great influence on their binding affinity to metal ions.

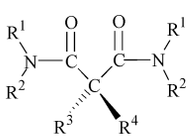

Fig. 1 Alkyl-substituted malonamides. *N*,*N*,*N*′,*N*′-Tetramethylmalonamide (TMMA: $R^1 = R^2$ = methyl, $R^3 = R^4$ = H); *N*,*N*′-dibutyl-*N*,*N*′-dimethylmalonamide (DMDBMA: R^1 = methyl, R^2 = butyl, $R^3 = R^4$ = H); *N*,*N*,*N*′,*N*′-tetra(isopropyl)malonamide (TiPMA: $R^1 = R^2$ = isopropyl, $R^3 = R^4$ = H); *N*,*N*,*N*′,*N*′-tetrahexylmalonamide (THMA: $R^1 = R^2$ = hexyl, $R^3 = R^4$ = H); 2-methyl-*N*,*N*,*N*′,*N*′-tetrahexylmalonamide (MeTHMA: $R^1 = R^2$ = hexyl, R^3 = methyl, R^4 = H); *N*,*N*,*N*′,*N*′-tetrahexyl-2,2-dimethylmalonamide (DMeTHMA: $R^1 = R^2$ = hexyl, $R^3 = R^4$ = methyl).

To extend these studies to more diamides and develop systematic relationships between the structural variations of the diamides and their binding properties, we have studied the complexation of Eu(III) with five more malonamides, including DMDBMA, TiPMA, THMA, MeTHMA and DMeTHMA (Fig. 1). These malonamides, together with TMMA studied in the previous work,[22] form two series of ligands with systematic changes in structure as follows: (1) TMMA–DMDBMA–THMA–TiPMA, where the bulkiness of the substitutional groups on the nitrogen atoms varies; (2) THMA–MeTHMA–DMeTHMA, where the substitution on the central carbon atom varies.

In this work, formation constants, enthalpy and entropy of the complexation between Eu(III) and the malonamides were determined by titration calorimetry and FT-IR spectroscopy in acetonitrile (AN) containing small amounts of dimethyl sulfoxide (DMSO). Luminescence spectroscopy was used to provide further insight into the complexation. The trends in the formation constants, enthalpy and entropy of complexation are discussed in terms of the structural variations of the malonamides.

Table 1 Formation constants, enthalpy and entropy of complexation between Eu(III) and alkyl-substituted malonamides (T = 25 °C, ionic strength = 0.1 M perchlorate)

	$Eu(ClO_4)_3$ in 10% DMSO/AN (by calorimetry)			$Eu(DMSO)_{7.2}(ClO_4)_3$ in AN (by FT-IR and luminescence)	
Malonamide	log $K^a \pm 3\sigma$	$\Delta H \pm 3\sigma$/ kJ mol^{-1}	$\Delta S \pm 3\sigma$/ J K^{-1} mol^{-1}	log $K \pm 3\sigma$	Normalized $I_{(^5D0 \longrightarrow {}^7F2)}$ [b]
TMMA [c]	1.34 ± 0.04	22.4 ± 0.8	101 ± 4	2.48 ± 0.05	4.4
DMDBMA	1.04 ± 0.08	29.6 ± 3.7	119 ± 14	2.08 ± 0.18	4.1
TiPMA	~0 ± 0.1	35.8 ± 8.6	120 ± 30	1.62 ± 0.09	4.0
THMA	0.55 ± 0.11	46.5 ± 9.7	166 ± 35	1.75 ± 0.15	3.9
MeTHMA	1.16 ± 0.08	9.8 ± 1.1	55 ± 5	1.97 ± 0.15	5.1
DMeTHMA		No complex		No complex	2.5

[a] K = [ML]/[M][L]/dm^3 mol^{-1}. [b] The intensity of the $^5D_0 \longrightarrow {}^7F_2$ transition is normalized against that of the $^5D_0 \longrightarrow {}^7F_1$ transition for each luminescence spectrum, [malonamide]/[Eu] = 4.4. [c] Data from ref. 22.

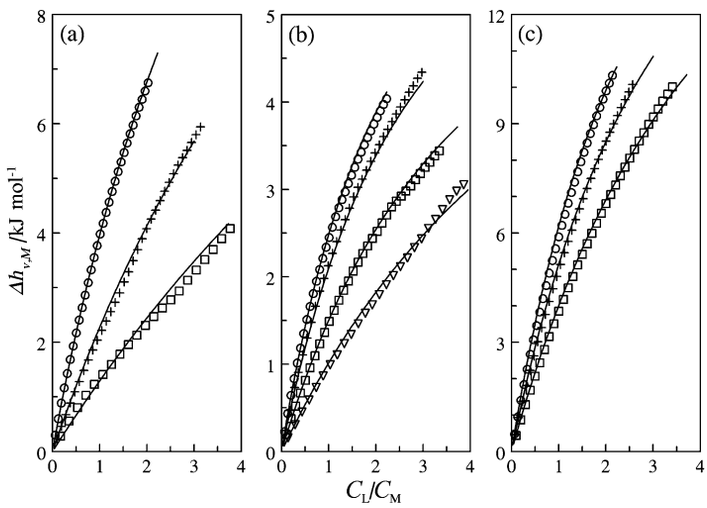

Fig. 2 Calorimetric titrations for the complexation of Eu(III) by malonamides in 10% DMSO/AN. (a) Eu/THMA: C_M^0 = 32.4 (○), 16.2 (+), 8.58 mmol dm^{-3} (□); (b) Eu/MeTHMA: C_M^0 = 33.85 (○), 25.39 (+), 16.92 (□), 8.46 mmol dm^{-3} (▽); (c) Eu/DMDBMA: C_M^0 = 33.35 (○), 25.01 (+), 16.68 mmol dm^{-3} (□). The lines are calculated by using the formation constants and enthalpy values in Table 1.

2 Results

2.1 Calorimetric studies: formation of Eu(III)–malonamide complexes in 10% DMSO/AN

The observed reaction heats for the complexation of Eu(III) by THMA, MeTHMA and DMDBMA are presented in Fig. 2 in the form of $\Delta h_{v,M}$ (defined in the Experimental section) as a function of the ligand to metal ratio (C_L/C_M = [malonamide]/[Eu]). The data indicate that the complexation of Eu(III) with these malonamides in 10% DMSO/AN is endothermic. The pattern of the titration curves (the curvature and the separation between titrations with different C_M^0) indicates that it is possible to calculate both the formation constants and the enthalpy of complexation from the calorimetric data. Various combinations of the complex species (*e.g.* EuL, EuL + EuL_2, *etc.*, where L stands for a malonamide) were used to model the systems. However, the least standard deviations were obtained when the titration curves were modeled with the formation of only one complex (EuL). The calculated values of the formation constants and the enthalpy are listed in Table 1. To test the goodness of the model, the formation constants and the enthalpy of complexation in Table 1 were in turn used to simulate the calorimetric titration curves. As shown in Fig. 2, the calculated curves provide good representations of the experimental data.

The calorimetric titrations of the Eu(III)–TiPMA system indicate that the complexation is also endothermic, but significantly weaker than the three systems shown in Fig. 2. The formation constant of Eu(TiPMA) in 10% DMSO/AN is calculated to be around 1 (log $K = 0 \pm 0.1$). In contrast to THMA, MeTHMA, DMDBMA, and TiPMA, no heat changes were observed for the Eu(III)–DMeTHMA system in 10% DMSO/AN. This observation implied two possible scenarios: either there was no complexation between Eu(III) and DMeTHMA in 10% DMSO/AN, or the enthalpy change of the complexation was near zero. Subsequent studies by FT-IR and luminescence spectroscopy supported the former.

2.2 FT-IR Studies: formation of Eu(III)–malonamide complexes in AN containing a small amount of DMSO ([DMSO]/[Eu] = 7.2)

FT-IR spectra (1550–1700 cm^{-1}) of the solutions of $Eu(DMSO)_{7.2}(ClO_4)_3$ and the six malonamide ligands in AN were obtained at different C_L/C_M (1.5–23). This is the region for the C=O stretching mode of the carbonyl groups in the diamides. The absorption bands for the C=O stretching in the free diamides are mostly around 1640–1650 cm^{-1} (Table 2). For all the six malonamides except DMeTHMA these bands are red-shifted in the presence of Eu(III) (Table 2), which could be attributed to the formation of Eu/malonamide complexes through coordination of the C=O groups. From the spectra, the formation constants of the complexes with all the malonamides except DMeTHMA are calculated and listed in Table 1.

The changes in the IR spectra due to the complexation are consistent with Byers' observation [17] for the complexation of La(III) with tetraethylmalonamide, where the C=O stretching mode of the "free" ligand was at 1645 cm^{-1} but shifted to 1613 cm^{-1} in the bound ligand. Edwards *et al.* also reported similar red-shifts of the C=O stretching bands when malonamides,

Table 2 The carbonyl stretching mode in the free and the bound malonamides

Complex system	C=O Stretching/cm^{-1}	
	free malonamide	bound malonamide
Eu/THMA	1637	1612
Eu/MeTHMA	1650	1610
Eu/TMMA	1648	1629
Eu/TiPMA	1638	1600
Eu/DMDBMA	1640	1620
Eu/DMeTHMA	1615	No complexation

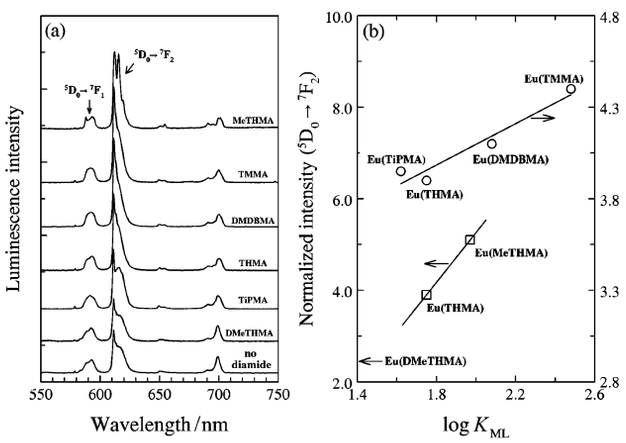

Fig. 3 (a) Luminescence emission spectra of $Eu(DMSO)_{7.2}(ClO_4)_3$ + malonamides in AN. [Eu] = 12.0 mmol dm^{-3} for all the spectra. [malonamide]/[Eu] = 4.4 for all the spectra except for the bottom spectrum where malonamide is absent. (b) The correlation between the complex formation constants and the normalized luminescence intensity of the $^5D_0 \longrightarrow {}^7F_2$ transition.

succinamides and glutaramides formed bidentate chelates with neodymium, uranium and thorium.[23]

For the Eu(III)/DMeTHMA system the feature of the absorption spectra of free DMeTHMA did not change when Eu(III) was present. No new bands were observed when C_L/C_M was changed from 1.5 to 23. Obviously, the IR data indicate that there is no complexation between Eu(III) and DMeTHMA in this solvent. This is not surprising since no heat effects were observed in the calorimetric titrations for this system.

2.3 Luminescence studies

While the FT-IR experiments were focused on the perturbation of the ligand C=O vibration upon complexation, luminescence spectroscopy provided further insight into the complexation by following the change in the europium luminescence induced by complexation. As shown in previous work,[22] the forbidden f–f excitation bands of Eu(III) in the UV region are weak and little affected by complexation with the malonamides. However, some of the luminescence emission bands in the visible region, originating from electronic transitions from the lowest excited state, $^5D_0$, to the ground state manifold, ^7F_J (J = 0–6), are sensitive to changes in the first coordination sphere.

The luminescence emission spectra of Eu(III) in the absence and in the presence of the malonamide ligands are shown in Fig. 3(a). The bottom spectrum is for a solution of $Eu(DMSO)_{7.2}(ClO_4)_3$ in AN without malonamides and is used as the reference. The other spectra are for solutions with malonamides where [malonamide]/[Eu] is constant (=4.4). As shown, the spectrum for DMeTHMA is identical to the reference spectrum, suggesting no interaction between Eu(III) and DMeTHMA in this solvent. This is consistent with the results obtained by FT-IR and calorimetry. In contrast to DMeTHMA, the presence of other malonamides results in changes in the emission spectra. In particular, the intensity of the $^5D_0 \longrightarrow {}^7F_2$ transition (around 610–630 nm) increases significantly compared to that in the reference spectrum. Attempts to correlate this change with the binding strength of the malonamide ligands are discussed in subsequent sections.

3 Discussion

3.1 Comparison of the formation constant in different solvents

The results in Table 1 indicate that the Eu(III)/malonamide complexes are about one order of magnitude weaker in 10% DMSO/AN (where [DMSO]/[Eu] ≥ 30) than in AN containing less DMSO (where [DMSO]/[Eu] = 7.2). This could be explained in terms of the solvation effect of DMSO in AN. Information in the literature[24,25] indicates that, in the absence of malonamide ligands, Eu(III) is preferentially solvated by DMSO in the mixture of DMSO/AN. When [DMSO]/[Eu] increases from 0 to about 7.7, DMSO molecules are quantitatively coordinated to Eu(III). When ths quotient is in the range of 7.7 to 12 there are equilibria between species containing seven, eight and nine coordinated DMSO molecules. When [DMSO]/[Eu] > 12, the nine-coordinated species, $Eu(DMSO)_9^{3+}$, is dominant with an average coordination number of 8.7 ± 0.5.[24] As a result, the formation of the Eu/malonamide complex (EuL) in 10% DMSO/AN ([DMSO]/[Eu] ≥ 30) requires the replacement of the strongly solvating DMSO from the coordination sphere of Eu(III). Consequently, the enthalpies of the formation of EuL in 10% DMSO are all endothermic and unfavorable to the complexation, ΔH ranging from 22.4 to 46.5 kJ mol^{-1} for TMMA, DMDBMA, TiPMA and THMA (Table 1).

On the other hand, in the system where [DMSO]/[Eu] = 7.2, the formation of EuL does not require the replacement of DMSO because the Eu(III) is not fully solvated by DMSO. Instead, some AN or ClO_4^- may be replaced, but the desolvation of AN or ClO_4^- consumes less energy because they are much weaker in solvating Eu(III). As a result, the enthalpy of the formation of EuL in this system should be more favorable to the complexation than that in 10% DMSO/AN. Though no enthalpy data were obtained from the FT-IR measurements in this work, the previous results for europium(III) complexation with TMMA and TMSA indicate that, indeed, the formation of EuL in AN with [DMSO]/[AN] = 7.2 has an enthalpy of −32 kJ mol^{-1} for both TMMA and TMSA.[22]

The degree of DMSO solvation not only affects the enthalpy of complexation, it has consequences in the entropy as well. As a bidentate ligand, one malonamide could replace two DMSO molecules from the primary coordination sphere of Eu(III). In the process of formation of EuL in 10% DMSO/AN, the loss of freedom of the diamide (mainly translational and rotational) is more than compensated by the concomitant gain in the entropy of two DMSO molecules free to move in the solvent. As a result, the entropy for EuL in 10% DMSO/AN is all positive and favorable to the complexation (Table 1). On the contrary, the entropy for EuL in AN with [DMSO]/[AN] = 7.2 is negative for TMMA and TMSA (−60 J K^{-1} mol^{-1}), as shown in the previous study.[22] In this solvent, it is probably the AN molecules, instead of DMSO, that are replaced by the malonamides. Considering that the structuring effect of the charged metal ion on the bulk solvent does not change substantially since no charge neutralization occurs when these complexes form, it is reasonable to presume that the released AN molecules do not gain excessive entropy once in the bulk solvent of AN. Consequently, the loss of translational and rotational entropy of the malonamides is only in part compensated, resulting in a negative entropy.

In summary, the complexation of Eu(III) with malonamides in the two solvents is consistent with the reaction schemes described in the previous study:[22] Scheme I (in

10% DMSO/AN), $Eu(DMSO)_9 + L \longrightarrow Eu(DMSO)_7L + 2$ DMSO (two DMSO molecules replaced, $\Delta H > 0$, $\Delta S > 0$); Scheme II (in AN with [DMSO]/[AN] = 7.2), $Eu(DMSO)_7 + L \longrightarrow Eu(DMSO)_7L$ (no DMSO molecules replaced, $\Delta H < 0$, $\Delta S < 0$). For these reactions the sign and the magnitude of the enthalpy and entropy changes primarily reflect the desolvation, which is consistent with the energetics of lanthanide complexation discussed in the literature.[26] Mainly due to the large difference in the desolvation energy, the complexation of Eu(III) with all the malonamides is weaker in 10% DMSO/AN than in AN with [DMSO]/[Eu] = 7.2 (Table 1). This is consistent with the previous results for the complexation of Eu(III) with TMMA and TMSA,[22] where the trend of binding strength in different solvents is: pure AN > AN ([DMSO]/[Eu] = 5.0) > AN ([DMSO]/[Eu] = 7.2) > 10% DMSO/AN > pure DMSO. The effect of europium(III) solvation by DMSO on the formation of Eu/TMMA and Eu/TMSA complexes has extensively been discussed in the previous study.[22]

3.2 Comparison of the binding strength between malonamides

Order of the binding strength. The formation constants in Table 1 indicate that, in either 10% DMSO/AN or AN with small amounts of DMSO ([DMSO]/Eu] = 7.2), the binding strength of the six malonamides with Eu(III) differs significantly, ranging from non-binding (for DMeTHMA) to moderately strong binding (for TMMA). As previously mentioned, these malonamides form two series of ligands with systematical changes in the structure. One series includes TMMA, DMDBMA, THMA and TiPMA, where the bulkiness of the substitutional groups on the nitrogen changes. The other series includes THMA, MeTHMA and DMeTHMA, where the substitution on the central carbon changes. As the data in Table 1 show, the formation constants change in the following orders: for the substitution on the nitrogen, TMMA > DMDBMA > THMA > TiPMA; for the substitution on the central carbon, MeTHMA > THMA > DMeTHMA.

The luminescence emission spectra shown in Fig. 3(a) provide further support for these orders. As pointed out by Bunzli and co-workers,[24,27] the $^5D_0 \longrightarrow {}^7F_1$ transition (around 590–600 nm) is a magnetic dipole transition and not affected by the environment of the fluorescent ion. So it is often used as an internal standard for intensity comparison. However, the hypersensitive $^5D_0 \longrightarrow {}^7F_2$ transition (around 610–630 nm) is very sensitive to the coordination of Eu(III). Accordingly, attempts have been made to correlate the luminescence intensity with the formation constants of the Eu/malonamide complexes. First, the intensity of the $^5D_0 \longrightarrow {}^7F_2$ transition was normalized against the intensity of the $^5D_0 \longrightarrow {}^7F_1$ transition for each spectrum (the normalized values are listed in Table 1). Then the normalized intensity was plotted against the formation constants (Fig. 3b). As shown in Fig. 3(b), log K_{ML} correlates well with the normalized $I(^5D_0 \longrightarrow {}^7F_2)$, meaning that the order of the binding strength observed by calorimetry and FT-IR is consistent with the order observed by luminescence. Indeed, the intensity of the hypersensitive transition $^5D_0 \longrightarrow {}^7F_2$ is a good measure of the strength of the interaction between Eu(III) and the malonamide ligands.

Effect of substitution on the nitrogen. The decrease in the formation constants of the Eu/malonamide complexes (TMMA > DMDBMA > THMA > TiPMA) suggests that the malonamides with larger substitutional groups on the nitrogen form weaker complexes with Eu(III). This could be explained in terms of the steric hindrance and the energy required for reorganization. To form the bidentate complex through the two carbonyl groups, some reorganization of the malonamide ligands and the solvent structure needs to occur. For example, the two carbonyl groups may have to be re-directed from a *trans* position to a nearly *cis* position to form the bidentate complex. Larger groups on the nitrogen probably cause higher steric hindrance to such reorganization, resulting in weaker complexation. Such a trend is observed for the series including TMMA, DMDBMA and THMA, as the substitutional groups become longer. From THMA to TiPMA, though the isopropyl group is "shorter", it may actually be "bulkier" due to its branched structure and could result in higher steric strain. As a result, TiPMA forms a weaker complex with Eu(III) than THMA.

It is interesting that the entropy of complexation increases from 101 J K^{-1} mol^{-1} for TMMA to 166 J K^{-1} mol^{-1} for THMA (Table 1), probably reflecting the higher gain in the degree of disorder caused by the longer substitutional groups.

Substitution on the central carbon. In the series THMA, MeTHMA and DMeTHMA, the methylene protons on the central carbon atom of THMA are replaced by one and two methyl groups. The strength of complexation decreases in the order: MeTHMA > THMA > DMeTHMA. It may seem to be surprising that MeTHMA forms a stronger complex than THMA because, based on the argument of steric hindrance discussed previously, the trend should be the opposite. Moreover, attempts to evaluate the energy of ligand structural reorganization by molecular mechanics calculations did not provide a satisfactory explanation for this trend.[28] However, it is known that the methyl substitution could increase the basicity of the carbonyl group due to its electron-donating nature. Higher basicity on the C=O could in turn result in higher binding ability with Eu(III). The much smaller positive enthalpy of the Eu/MeTHMA complex (9.8 kJ mol^{-1}, compared to 22–46 kJ mol^{-1} for other malonamides, Table 1) seems consistent with such an argument and implies that the interaction between Eu(III) and MeTHMA may be different from other malonamides. At present, data on the basicity of these malonamides in AN are not available. However, information on the analogous malonates in aqueous solutions may provide insight into the effect of alkyl substitution on the basicity of the carbonyl groups. The pK_{a1} of malonic acid, methylmalonic acid and dimethylmalonic acid are 5.28, 5.40 and 5.68 (I = 0.1 mol dm^{-3}, 25 °C), respectively,[29] reflecting the increase of basicity due to successive methyl substitutions on the central carbon atom.

Of course, there may still be steric hindrance due to the methyl substitution, which would weaken the complexation. In the case of MeTHMA, this effect may not be as significant as the effect of the increase in the basicity that would strengthen the complexation. Consequently, MeTHMA forms a stronger complex with Eu(III) than THMA. However, in the case of DMeTHMA, the weakening effect of steric hindrance due to two methyl groups may become more significant than the strengthening effect of the increased basicity. As a result, the complexation between DMeTHMA and Eu(III) is too weak to be observed.

The effect of the length of the carbon backbone on the complexation has been discussed in a previous study of TMMA and TMSA.[22] TMMA forms stronger complexes with Eu(III) than TMSA in either 10% DMSO/AN or AN with small amounts of DMSO ([DMSO]/[Eu] = 7.2). This is attributed to the difference in steric strain induced by the complexation and an entropy effect.[22]

4 Experimental

Precautions were taken to obtain and maintain the lowest water content in the systems throughout the experiments by working under an inert atmosphere of dry nitrogen or argon. Solutions were prepared in a controlled atmosphere chamber or a glove bag filled with dry nitrogen or argon. Before being introduced into the chamber, the apparatus and non-volatile samples were degassed in a transport that was evacuated and purged with dry nitrogen or argon at least three times. All the experiments were

conducted at 25 °C and the ionic strength was maintained at 0.1 mol dm^{-3} with tetraethylammonium perchlorate.

4.1 Chemicals

Fresh anhydrous solvents (unopened bottles), including AN and DMSO (both from Aldrich, water content < 0.005%), were used for the experiments without further treatment. 10% DMSO/AN (w/w) was prepared by weighing and mixing calculated amounts of DMSO and AN under an atmosphere of dry argon.

The procedures for preparing anhydrous tetraethylammonium perchlorate and europium perchlorate were described in previous publications.[22,30] **CAUTION**: in the preparation of europium perchlorate, extreme precautions must be taken to avoid using a large or even moderate excess of perchloric acid because this can be the origin of serious accidents.[31] The quantity of Eu in the solid salt and in the stock solutions was determined by complexometry with EDTA.[32] For the calorimetric titrations, working solutions of Eu were prepared by appropriate dilution of the stock with 0.1 mol dm^{-3} tetraethylammonium perchlorate. For the FT-IR experiments, the stock solution was prepared by dissolving a well characterized adduct compound, $Eu(DMSO)_{7.2}(ClO_4)_3$ ($M = 1013.1$), in AN. The compound was prepared according to the procedures described elsewhere[33] and characterized by elemental analysis and complexometry.

The malonamides, including THMA, DMDBMA, TiPMA, MeTHMA, DMeTHMA and TMMA, were supplied by Drs B. Rapko and M. Alnajjar of the Pacific Northwest National Laboratory, Richland, Washington, USA. The compounds were characterized by ^1H and ^{13}C NMR, IR, and GC-MS. Their purity was estimated to be >99%. Stock solutions of the malonamides (usually 300–400 mmol dm^{-3}) were prepared by dissolving weighed amounts in the appropriate solvents.

4.2 Titration calorimetry

All calorimetric experiments were carried out at 25.0 ± 0.1 °C with an isoperibol titration calorimeter (Calorimetry Sciences Corp.), equipped with a 25 mL titration vessel. Operations including filling the burette with the ligand solutions and loading the europium solutions in the titration cup were all carried out in a controlled atmosphere chamber or a plastic bag filled with dry nitrogen or argon.

10% DMSO/AN (w/w) was used as the solvent for the calorimetric experiments to study the complexation of Eu(III) with DMDBMA, TiPMA, THMA, MeTHMA and DMeTHMA. This is the solvent previously used in the study of the complexation between Eu(III) and two diamides (TMMA and TMSA).[22] Using this solvent allows the comparison of the formation constants obtained in this work with those obtained previously. Besides, there is a considerable amount of information in the literature on the lanthanides/DMSO/AN systems[24] that allows a thorough understanding of metal solvation in this solvent. In these titrations, the DMSO is in large excess with respect to Eu ([DMSO]/[Eu] ≥ 30). For each malonamide, usually 3 to 4 titration runs with different C_M^0 (the initial concentration of Eu in the cup) were performed to achieve better statistics in the calculation of formation constants and reaction enthalpies.

The heats of formation of the Eu(III)/malonamide complexes in 10% DMSO/AN were determined by adding a ligand solution of concentration C_L^0 at a constant rate (0.2 mL min^{-1}) from the burette to a europium solution of concentration C_M^0 in the reaction vessel. C_L^0 is usually in the range of 300 to 500 mmol dm^{-3} and C_M^0 in the range of 7 to 33 mmol dm^{-3}. For each titration run, n experimental values of the total heat produced in the reaction vessel ($Q_{ex,j}$, $j = 1$ to n) were calculated as a function of the volume of the added titrant. These values were corrected for the heat of dilution of the titrant ($Q_{dil,j}$), which was determined separately. No correction was made for the heat of dilution of the titrate because it was found to be negligible in the metal concentration range used. The net reaction heat at the jth point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. Then the total heat per mole of metal, $\Delta h_{v,M}$, was calculated by dividing the net reaction heat by the number of moles of metal in the calorimeter vessel.[34] The formation constants of the identified complexes, the enthalpy and entropy changes of the complexation were calculated by using a FORTRAN program MQF 90[35] with $\Delta h_{v,M}$ as the error-carrying variable.

4.3 FT-IR Spectroscopy

FT-IR spectroscopy was used to determine the formation constants of the Eu(III)/malonamide complexes in AN containing small amounts of DMSO ([DMSO]/[Eu] = 7.2). The IR spectra were recorded under dry nitrogen purge at 25 ± 1 °C on a Sirius 100 FT-IR spectrometer (Mattson Instruments, Inc.) with a 2 cm^{-1} resolution and 256 scans. Cells with barium fluoride windows were used. The quantitative measurements were made with a single cell, the exact optical path of which was determined to be 30.8 μm by the interference fringe method.[36] The cells were filled with the sample solutions in a glove bag, tightly closed, and transferred to the spectrometer with a sealed container. The spectra of pure AN and the sample solutions were recorded separately, ratioed against the background and converted into absorbance units. The spectrum of pure AN was then numerically subtracted from the sample solution spectra to obtain the difference spectra. The spectra in the region from 1550 to 1700 cm^{-1} (*i.e.* the region for C=O stretching) were analyzed with a modified SQUAD program[37] to obtain the formation constants of the Eu(III)–malonamide complexes.

4.4 Luminescence spectroscopy

Luminescence measurements were performed on a FluoroMax-2 spectrometer (Jobin Yvon-Spex Instruments S.A., Inc.) with a standard 1 cm quartz fluorometer cell. The emission spectra of europium solutions in the region from 500 to 750 nm were obtained from the $^7F_0 \longrightarrow {}^5L_6$ excitation at 395 nm.

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